SOUTHERN CALIFORNIA PARTICLE SUPERSITE

Progress Report for Period October 1, 2003 – December 30, 2003

United States Environmental Protection Agency

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1. Introduction

The overall objective of the Southern California Particle Supersite is to conduct research and monitoring that contributes to a better understanding of the measurement, sources, size distribution, chemical composition and physical state, spatial and temporal variability, and health effects of suspended particulate matter (PM) in the Los Angeles Basin (LAB). This report addresses the period from October 1, 2003 – December 30, 2003. It is divided into 9 sections, each addressing a specific research area. Furthermore, a major portion of the information included in this report has been either submitted or accepted for publication in peer-reviewed journals. Below is a list of manuscripts either submitted or accepted for publication which was produced through the Southern California Supersite funds and in which the EPA Supersite program has been acknowledged.

2. Publications

The Southern California Particle Supersite has been acknowledged so far in the following publications:

1. Misra, C., Geller, M., Sioutas, C and Solomon P. "Development and evaluation of a continuous coarse particle monitor". *Journal of Air and Waste Management Association*, 51:1309-1317, 2001
2. Geller, M.D., Kim, S. Misra, C., Sioutas, C., Olson, B.A and Marple, V.A. "Methodology for measuring size-dependent chemical composition of ultrafine particles " *Aerosol Science and Technology*, 36(6): 748-763, 2002
3. Misra, C., Kim S., Shen S. and Sioutas C. "Design and evaluation of a high-flow rate, very low pressure drop impactor for separation and collection of fine from ultrafine particles". *Journal of Aerosol Science*, 33(5): 735-752, 2002
4. Li, N., Kim, S., Wang, M., Froines, J.R., Sioutas, C. and Nel, A. "Use of a Stratified Oxidative Stress Model to Study the Biological Effects of Ambient Concentrated and Diesel Exhaust Particulate Matter". *Inhalation Toxicology*, 14(5): 459-486, 2002

5. Zhu, Y., Hinds, W.C., Kim, S and Sioutas, C. "Concentration and Size Distribution of Ultrafine Particles near a Major Highway". Journal of Air and Waste Management Association, 52:1032-1042, 2002
6. Singh, M., Jaques, P. and Sioutas, C. "Particle-bound metals in source and receptor sites of the Los Angeles Basin". Atmospheric Environment, 36(10): 1675-168, 2002
7. Kim, S., Shi, S., Zhu, Y., Hinds, W.C., and Sioutas, C. "Size Distribution, Diurnal and Seasonal Trends of Ultrafine Particles in Source and Receptor Sites of the Los Angeles Basin". Journal of Air and Waste Management Association, 52:174-185, 2002
8. Misra, C., Singh, M., Hall, P. and Sioutas, C. "Development and evaluation of a personal cascade impactor sampler (PCIS)". Journal of Aerosol Science, 33(7), 1027-1047, 2002
9. Eiguren-Fernandez A., Miguel A.H, Jaques, P. and Sioutas, C. "Evaluation of a Denuder-MOUDI-PUF Sampling System to Determine the Size Distribution of Semivolatile Polycyclic Aromatic Hydrocarbons in the Atmosphere". Aerosol Science and Technology, 37: 201-209, 2003
10. Fine, P.M., Hering, S.V., Jaques P.A. and Sioutas, C. "Performance Evaluation and Field Use of a Continuous Monitor for Measuring Size-Segregated PM2.5 Particulate Nitrate". Aerosol Science and Technology, 37: 342-354, 2003
11. Singh, M., Misra, C., and Sioutas, C. "Field Evaluation of a Particle Monitor for Size-Dependent Measurement of Mass and Chemical Composition of Individual Exposures to PM". *Atmospheric Environment*, 37(34), 4781-4793, 2003.
12. Shen, S., Zhu, Y., Jaques PA and Sioutas C. "Evaluation of the SMPS-APS system as a Continuous Monitor for PM2.5 and PM10". Atmospheric Environment, 36, 3939-3950, 2002
13. Zhu, Y., Hinds, W.C., Kim, S., Shen, S. and Sioutas, C. "Study on Ultrafine Particles and other Vehicular Pollutants near a Busy Highway". Atmospheric Environment. 36, 4375-4383, 2002
14. Misra, C., Geller, M.D., Solomon, P.A. and Sioutas, C. "Development of a PM10 Inertial Impactor for Coarse Particle Measurement and Speciation." Aerosol Science and Technology, 37:271-282, 2003
15. Zhu, Y., Hinds, W.C., Kim, S., Shen, S. and Sioutas, C. "Seasonal Trends of Concentration and Size Distributions of Ultrafine Particles Near Major Freeways in Los Angeles". Aerosol Science and Technology, in press, April 2003
16. Misra, C., Geller, M., Fine, P.M.. and Sioutas, C. "Development and Evaluation of an Ultrafine Particle Concentrator Facility for Human Exposures". *Aerosol Science and Technology*, 38, 27-35, 2004.
17. Gong, H.Jr, Linn, W.S., Sioutas, C., Terrell S.L., Clark, K.W., Anderson K.R and Terrell, L . "Controlled Exposures of Healthy and Asthmatic Volunteers to Concentrated Ambient Fine Particles in Los Angeles". Inhalation Toxicology, 15(4), 305-325.
18. Li, N., Sioutas, C , Froines, J.R., Cho, A., Misra, C and Nel, A., "Ultrafine Particulate Pollutants Induce Oxidative Stress and Mitochondrial Damage" *Environmental Health Perspectives*, 111 (4), 455-460, 2003

19. Chakrabarti, B., Singh, M and Sioutas C. “Development of a Continuous Monitor For Measuring the Mass Concentration of Ultrafine PM.” Aerosol Science and Technology, in press, January 2003
20. Jaques, P.A., Ambs, J.L. and Sioutas, C. “Field Evaluation Of The Differential TEOM® Monitor For Continuous PM2.5 Mass Concentrations “. Submitted to Aerosol Science and Technology, September 2002
21. Zhu, Y., Hinds, W.C. and Sioutas, C. “Vertical Profile of Ultrafine Particles in the Vicinity of a Major Highway”. Submitted to Atmospheric Environment, December 2002
22. Fine, P.M., Si, S., Geller, M.G., and Sioutas, C. “Diurnal and Seasonal Characteristics and Size of Ultrafine PM in Receptor Areas of the Los Angeles Basin”. Aerosol Science and Technology, in press, 2003
23. Chakrabarti, B., Fine, P.M, Delfino R.J. and Sioutas C. “Performance Evaluation of an active personal DataRAM PM2.5 mass monitor (Thermo Anderson pDR-1200) designed for continuous personal exposure measurements” Submitted to Atmospheric Environment, February 2003
24. Yu, R.C., Teh, H.W., Sioutas, C. and Froines, J.R. “Quality Control of Semi-Continuous Mobility Size-Fractionated Particle Number Concentration Data”. Submitted to Atmospheric Environment, February 2003
25. Miguel, A.H., Eiguren-Fernandez, A., Jaques, P.A., Mayo, P.R. and Sioutas, C. “Seasonal variation of the particle size distribution of polycyclic aromatic hydrocarbons and of major aerosol species in Claremont, California” Submitted to Atmospheric Environment, February 2003
26. Sardar, S.B., Fine, P.M., Jaques, P.A., Sioutas, C. “Seasonal and Spatial Variability of the Size-Resolved Chemical Composition of $PM_{2.5}$ in the Los Angeles Basin.” Submitted to Atmospheric Environment, June 2003
27. Geller, M.D., Fine, P.M. and Sioutas* C. “ The Relationship Between Real-Time and Time-Integrated Fine and Coarse Particle Concentrations at an Urban Site in Los Angeles, CA”. *Journal of Air and Waste Management Association*, in press, November 2003

28. Eiguren-Fernandez, A., Miguel, A.H., Froines, J.R., Thurairatnam, S., Avol, E. “Seasonal and Spatial Variation of Polycyclic Aromatic Hydrocarbons in Vapor-Phase and $PM_{2.5}$ in Southern California Urban and Rural Communities” Submitted to *Atmospheric Environment*, June 2003.
29. Reisen, F., Wheeler, S. and Arey, J. “Methyl- and Dimethyl-/Ethyl-Nitronaphthalenes Measured in Ambient Air in Southern California” accepted by Atmospheric Environment, June 2003.

30. Sardar, S.B., Fine P.M., Jaques, P.A and Sioutas*. C. “Seasonal and Spatial Variability of the Size-Resolved Chemical Composition of $PM_{2.5}$ in the Los Angeles Basin” Submitted to *Journal of Geophysical Research*, December 2003

31. Jaques, P.A., Ambs, J.L., Hering, S.V., Fine, P.M. and Sioutas*, C. " Field Assessment of the Dynamics of Particulate Nitrate Vaporization Using

Differential TEOM® and Automated Nitrate Monitors ". *Atmospheric Environment*, in press, October 2003

32. Fine, P.M., Chakrabarti, B, Krudysz M., Schauer J.J. and Sioutas*, C. “Seasonal, Spatial, and Diurnal Variations of Individual Organic Compound Constituents of Ultrafine and Accumulation Mode PM in the Los Angeles Basin”. *Environmental Science and Technology*, accepted for publication, November 2003.

33. Sardar, S.B., Fine P.M., and Sioutas*. C. “The Relationship Between Particle Number and Co-pollutant Concentrations in the Los Angeles Basin” Submitted to *Journal of Air and Waste Management Association*, October 2003

34. Zhang, K.M., Wexler, A.S., Zhu, Y., Hinds, W.C. and Sioutas, C. “Evolution of Particle Number Distributions Near Roadways. Part II: The “Road-to-Ambient Process”. Submitted to *Atmospheric Environment*, December 2003.

35. Miguel, A.H., Cho A.K., Sioutas C., Schmitz, D.A., Kumagai Y., Misra C., Singh M., and Froines, J.R. “DTT Activity Assay for Measurement of the Oxidative Stress Inducing Capacity if Polycyclic Aromatic Compounds in the Atmosphere”. Submitted to *Polycyclic Aromatic Compounds*, November 2003.

36. Zhao, Y., Bein, K.J., Wexler, A.S., Misra, C., Fine, P.M. and C. Sioutas* , C. “Using a Particle Concentrator to Increase the Hit Rates of Single Particle Mass Spectrometers”. Submitted to *Journal of Geophysical Research*, December 2003

3. PIU Sampling Location and Status

A key feature of our Supersite activities has been in the ability to conduct state-of the art measurements of the physiochemical characteristics of PM in different locations of the Los Angeles basin (LAB). We originally proposed a 2.5-year repeating cycle of measurements at five locations. Each location has been scheduled to sample during a period of intense photochemistry (defined approximately as May-October) and low photochemical activity (defined as the period between November-April). During the period of this progress report, we've continued PM sampling with the Particle Instrumentation Unit (PIU) at the University of Southern California (USC), the fifth Southern California Supersite location, beginning September 2002. The site is located about one mile directly south of downtown Los Angeles and the 10 Freeway, which runs east to west, and is about 100 meters directly east of the 110 Freeway. The site is embellished with typical urban sources: centralized within a major congested urban center; adjacent to several 2–7 story buildings; adjacent to pedestrian and local traffic as well as central arteries; and near building and road construction projects. Since the site is about 15 miles directly east north east of the ocean, prevailing winds are primarily from the west and southwest during most of the daytime when mobile and stationary emission sources may be expected to predominate. However, the nearby relatively large buildings can also disturb the winds, affecting urban canyon and wake properties. These factors consist of turbulent winds and updrafts that may confound local measurements of regional wind trajectories, and increase the delivery of local sources (e.g., construction debris, and larger settled particles from road related vehicle wear-and-tear) in addition to the close-by 110 Freeway. Several studies are being conducted as we enter the third quarter at the USC site to investigate local source contributions in addition to the regional transported emissions that may generally come from the west freeways.

We have completed all Metal/Element speciation, Ion, and EC/OC analysis for integrated samples, through to the end of October. In early June, we finalized size integrated on-line measurements of particulate nitrate and carbon using the Integrated Collection and Vaporization System (ICVS) developed by Aerosol Dynamics Inc. Additionally, paired semi-continuous PM2.5 measurements using a prototype Differential TEOM, designed to measure "non-artifact" laden mass, has been completed. Two continuous BAM monitors continue to operate: one, with the standard PM2.5 inlet, the second with an ultrafine inlet (designed at the USC lab). Coupled with our USC-TEOM coarse monitor, time-integrated mass measurements are being compared to those by our SMPS-APS, MOUDI, Partisol, and other filter mass samplers for longer sample integrals, overall, resulting in paired integrated semi-continuous, diurnal, and 24-hour mass measurements of coarse, fine, and ultrafine PM.

We have continued to make our mobile particle trailer available for co-located exposure studies. The following health studies have been supported by the Supersite measurements: In vitro studies undertaken by Drs. Andre Nel and Arthur Cho (UCLA) investigating the hypotheses that organic constituents associated with PM, including quinines, other organic compounds (PAHs, nitro-PAHs, and aldehydes/ketones) and metals are capable of generating reactive oxygen species (RQS) and acting as electrophilic agents. These are ongoing studies. Animal inhalation toxicology studies using Concentrated Ambient Particulates (CAP) investigating the hypotheses that atmospheric chemistry is important in the toxicity of PM and co-pollutants, airway injury and cardiovascular effects will be greater at receptor sites downwind of source sites along the mobile source trajectory in the Los Angeles basin. Led by Drs. Harkema (University of Michigan), Kleinman (UC Irvine), Froines, and Nel (UCLA), these co-located studies have commenced during our first month at the USC site and have continued periodically to the present. A demonstrative-level cooperative project of the California Air Resources Board and the Supersite was initiated during the winter of 2003 to evaluate the nature of PM and gaseous pollutants in various microenvironments of Southern California, especially those impacted by vehicular traffic. Gaseous pollutants evaluated included carbon monoxide, carbon dioxide, and oxides of nitrogen using advanced monitoring equipment including ultrafine PM counters and sizers as well as carbon, PM 2.5, and PAH monitors placed in an electrically powered Toyota RAV4. Data reporting resolution was one minute or less with operations of the study closely linked to the Supersite, its instrumentation and staff.

4. Time integrated, size fractionated mass and chemical speciation for five sites in the Los Angeles Basin

Sampling and chemical analysis of PM for the month of July to September 2003 were done at USC PIU. The results for this report are given in the Figures 1 through 6. In Figure1 at USC the coarse mode dominated the PM followed by the accumulation mode. The PM levels increased in summer as compared to the winter months. In Fig 2 at USC nitrate and metals dominates the coarse mode for the months of August and September 2003. During these months nitrate contribution to the coarse mode increased as compared to the winter months resulting from photochemical formation of nitrate particles. In the summer months, sulfate is also observed to be high and have resulted from particle formation by photochemistry at this site. In Figure 3, nitrate, sulfate and organics dominated the accumulation mode. In this mode during summer the sulphate level has shown an increase as compared to the earlier winter months, which have resulted from photochemical formation of sulphate particles. The ultrafine mode (Fig 4) is dominated by OC as for the rest of the months and sites. Interestingly contributions of sulphate and metals are found during the month of August and September at USC in the ultrafine mode. The increase of sulphate is due to the photochemistry involved while the metals in this site may have been the contributions of lube oils from traffic at USC, which is a source site. During this two months nitrate is not detected at USC. In Figure 5 at USC and in the months of August and September the OC concentration is more in ultrafine and accumulation mode in line with results previously narrated. Both the months of August and September at USC showed the predominance of EC (Fig 6) in the ultrafine mode as expected because USC is a source site and the EC is emitted in primary emissions from diesel vehicles in this mode. A high coefficient of statistical determination, R^2 of 0.63, was found for USC between EC and OC. USC is a source site and this high R^2 is indicative of primary emissions from vehicular source.

Currently sampling is going on at USC PIU and new results will be added during the presentation of next report.

Table 1

Site	Period of Sampling
Downey	Oct 2000 – Feb 2001
Riverside	Feb 2001 – June 2001
Rubidoux	June 2001 – Sept 2001
Claremont	Sept 2001 – Aug 2002
USC	Oct 2001 – Ongoing

Table 2: Averaged OC/EC ratios and correlation coefficients at source and receptor sites

Source site	**Average and Std Dev**	**Range**	**R^2**
Downey	5.08 ± 2.3	2.7 – 9.57	0.81
USC	4.12 ± 1.14	3.26 – 7.42	0.63
Receptor site	**Average and Std Dev**	**Range**	**R^2**
Rubidoux	7.78 ± 1.76	6.6 – 8.9	0.57
Riverside	6.05 ± 3.55	3.6 – 15.2	0.64
Claremont	14.84 ± 8.2	4.4 – 35.7	0.38

The correlation coefficients between measured metal concentrations in the coarse and fine (accumulation plus ultrafine) modes at receptor and source sites are given in Table 3. Only the more significant correlations are included (R^2 > 0.6). In the coarse mode at the source sites, high correlations are observed for many of the elements. The highest correlations suggest a common source of Al and Si, and a related source of Fe, Ti, Mn, Zn, and Cu. The major source of coarse particles is soil and road dust, and these elements can all be of crustal origin. In the fine mode and at the source sites, the degree of correlation among elements drops significantly. Fine particles have more varied sources than coarse particles, and thus inter-element correlations are reduced by varying contributions of multiple sources of the same element. The results show moderately high correlations among some metals (Fe, Si, Mn, Zn), which may originate from crustal, vehicular, or industrial sources. Additional high correlation coefficients were observed in the coarse mode at the receptor sites between Al and Si and some other crustal metals indicating a soil/road dust source. Unlike the coarse mode, no significant correlations were observed in the fine mode at the receptor sites. In general, less correlation is expected at the downwind receptor sites due to the potential influence of a greater variety of sources upwind.

Table 3: Correlations between 24-h averaged mass concentrations of selected metals at source and receptor sites (only cases when R^2 > 0.6 are given)

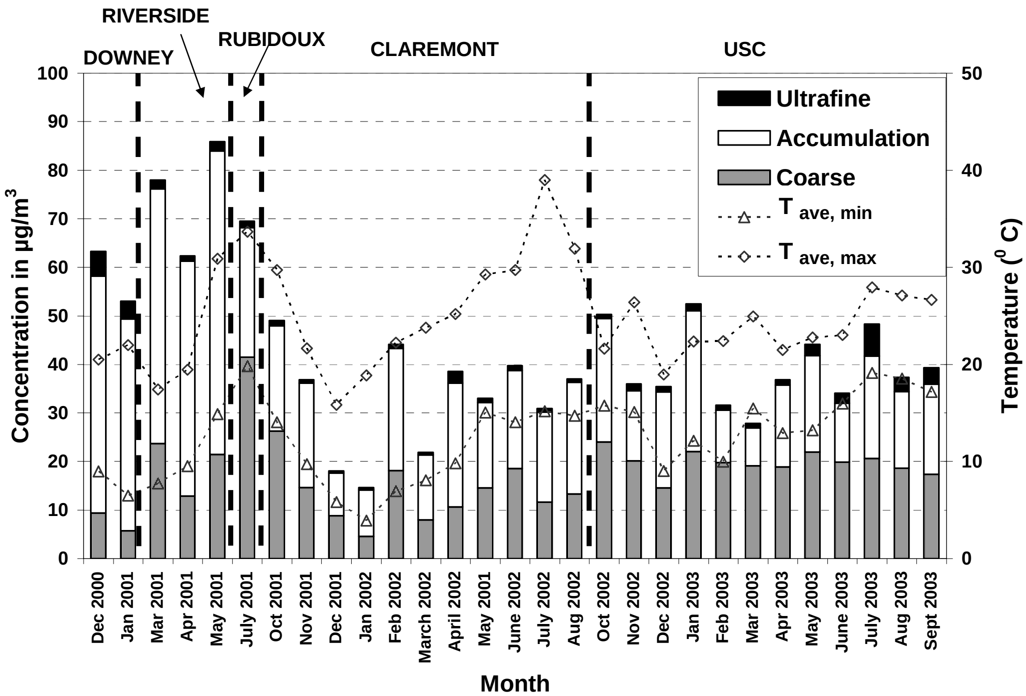
Source Sites (Downey/USC)

Coarse mode						Fine mode					
Metal	Metal	n	R^2	Slope	Intercept (μg/m^3)	Metal	Metal	n	R^2	Slope	Intercept (μg/m^3)
Al	Si	36	0.98	2.16	-0.0029	Si	Fe	36	0.88	1.37	0.0400

Al	Fe	36	0.81	2.04	0.0146	Si	Mn	35	0.79	0.09	0.0011
Al	Ti	36	0.76	0.13	0.0008	Si	Zn	35	0.76	0.06	0.0169
Al	Mn	36	0.79	0.13	-0.0003	Fe	Ti	35	0.88	0.04	0.0154
Al	Zn	36	0.6	0.03	0.0020	Fe	Mn	35	0.77	0.027	0.0063
Si	Fe	36	0.84	1.09	0.0201	Fe	Cu	35	0.72	0.033	0.0034
Si	Ti	35	0.77	0.03	0.0010	Fe	Zn	35	0.79	0.062	0.0241
Si	Mn	35	0.69	0.07	0.0001	Mn	Zn	36	0.81	2.85	0.0133
Si	Zn	35	0.73	0.04	0.0015						
Fe	Ti	35	0.83	0.10	-0.0019						
Fe	V	35	0.85	0.00	-0.0017						
Fe	Mn	35	0.88	0.02	-0.0003						
Fe	Cu	35	0.95	0.06	-0.0028						
Fe	Zn	35	0.86	0.03	0.0008						
Ti	V	35	0.81	0.06	-0.0019						
Ti	Mn	35	0.91	0.27	0.0014						
Ti	Cu	35	0.88	0.56	-0.0017						
Ti	Zn	35	0.88	0.39	0.0013						
V	Mn	35	0.79	1.22	0.0022						
V	Cu	35	0.92	4.79	0.0036						
V	Zn	35	0.78	2.86	0.0077						

Receptor Sites (Claremont/Riverside/Rubidoux)

Coarse mode					
Metal	**Metal**	**N**	**R^2**	**Slope**	**Intercept ($\mu g/m^3$)**
Al	Si	55	0.92	0.94	0.0200
Al	Fe	55	0.64	0.88	0.1800
Al	Mn	55	0.81	0.02	0.0013
Al	Cu	55	0.66	0.01	0.0031
Mn	Cu	55	0.71	0.44	0.0026



RIVERSIDE
RUBIDOUX
DOWNEY
CLAREMONT
USC
Ultrafine
Accumulation
Coarse
T ave, min
T ave, max
Concentration in µg/m3
Temperature (0 C)
Month
Dec 2000
Jan 2001
Mar 2001
Apr 2001
May 2001
July 2001
Oct 2001
Nov 2001
Dec 2001
Jan 2002
Feb 2002
March 2002
April 2002
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Figure 1

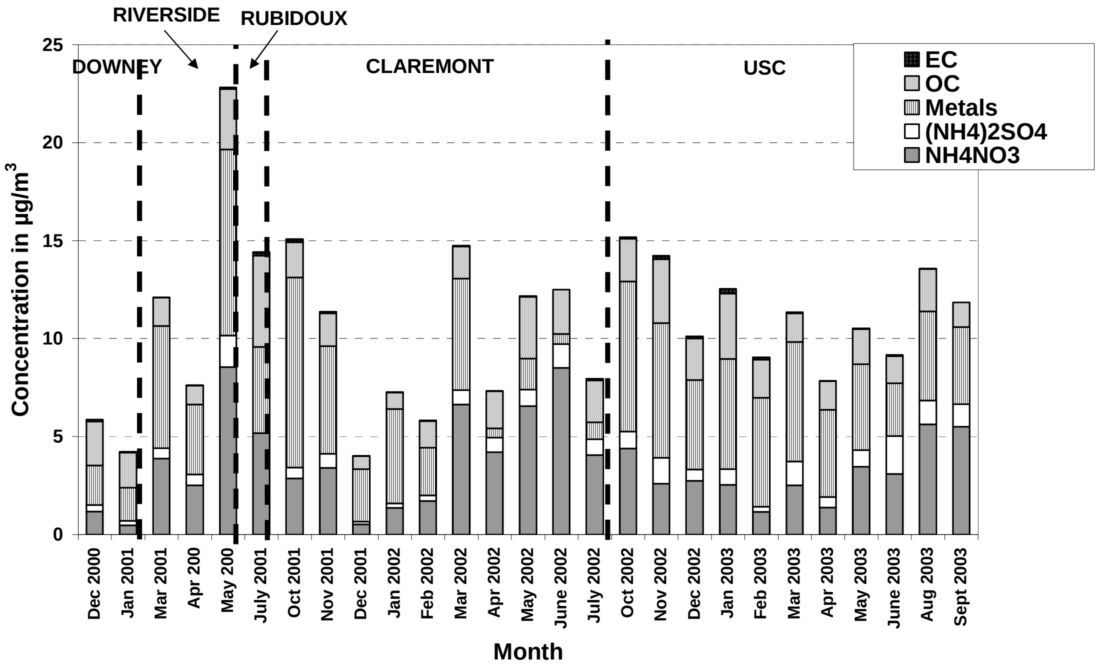

Figure 2

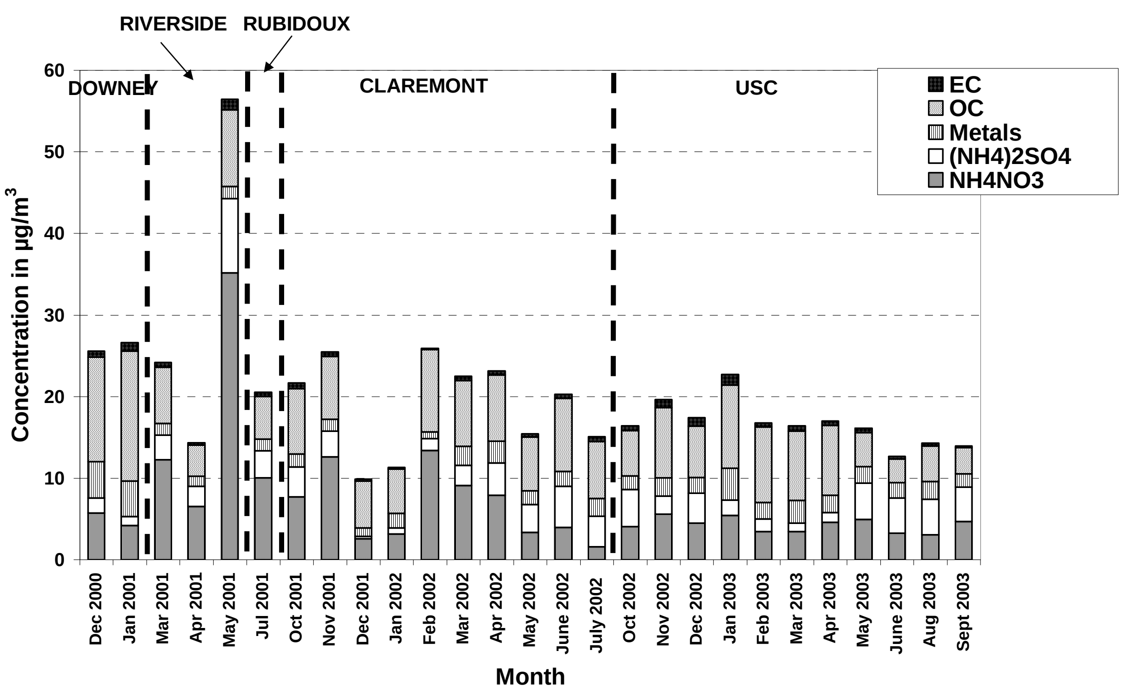

Figure 3

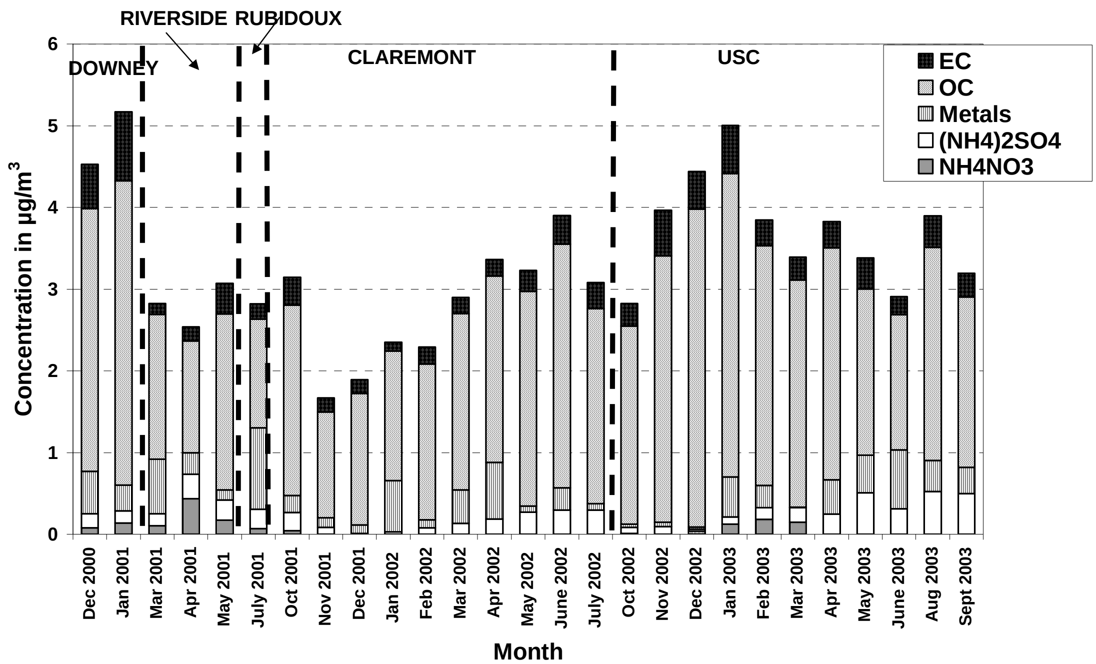

Figure 4

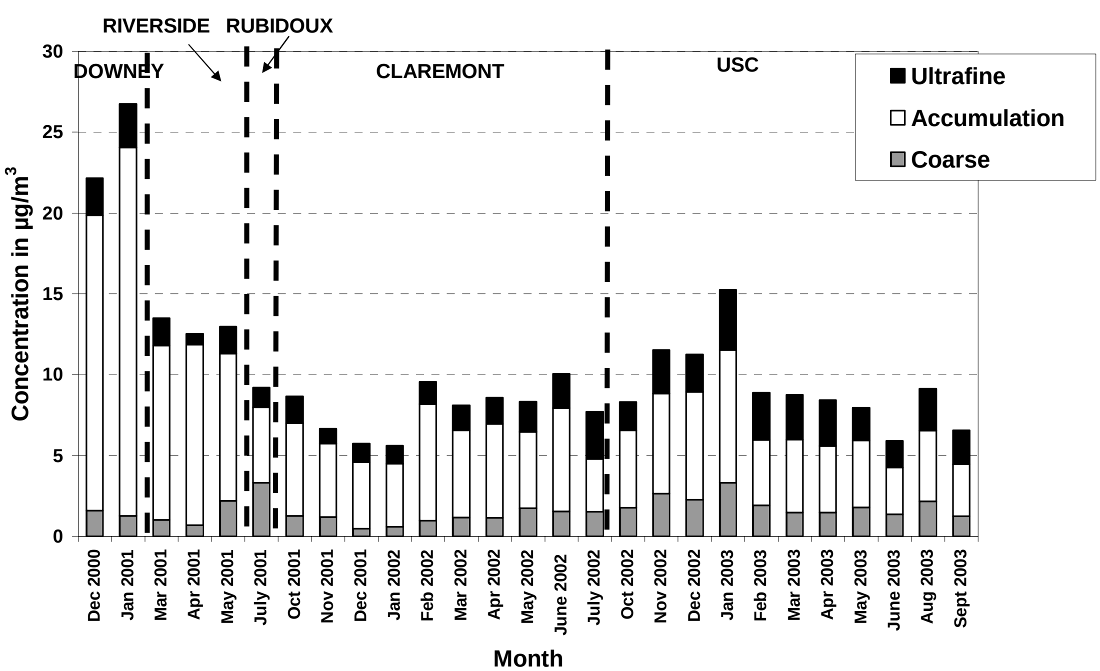

Figure 5

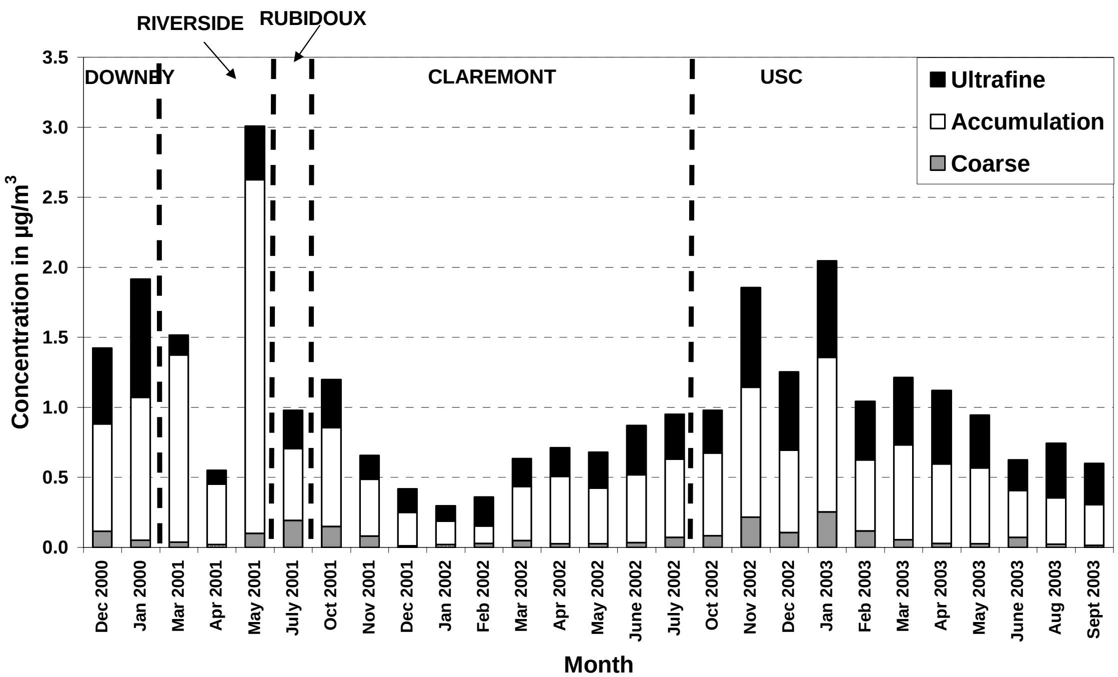

Figure 6

5. Characterization of PAH and PAH-Derivatives

Results of Ambient Measurements

A manuscript entitled "Atmospheric Reactions Influence Seasonal PAH and Nitro-PAH Concentrations in the Los Angeles Basin" by Fabienne Reisen and Janet Arey and describing our results from sampling in the summer at Los Angeles (August 12-16, 2002) and Riverside (August 26-30, 2002) and in the winter at Los Angeles (January 13-17, 2003) and Riverside (January 27-31, 2003) will shortly be submitted for publication.

Ambient measurements of polycyclic aromatic hydrocarbons (PAHs) and nitro-PAHs were carried out in Los Angeles, CA, a source site and in Riverside, CA, a downwind receptor site during August 2002 and January 2003. To augment our current understanding of atmospheric formation of nitro-PAHs, four sampling periods were employed to study the diurnal variations of these compounds. The sampling consisted of three daytime samples of 3.5 hrs each and one nighttime sample of 11.5 hrs. The sampling times (given in local time) were chosen to emphasize direct emissions (early morning, 7-10:30, labeled "Morning" on Figure 1), the period at highest expected photochemical activity (11-14:30, labeled "Day" on Figure 1), the period around sunset when NO3 chemistry could begin (15-18:30, labeled "Evening" on Figure 1) and an overnight sample (19-6:30, labeled "Night" on Figure 1).

The PAH and nitro-PAH data for the summer and winter sampling campaigns are given in Tables 1 and 2, respectively (note all abbreviations used for the PAH and nitro-

PAH are defined on Table 1). The PAH concentrations were highest in Los Angeles during January, as a result of traffic input at this source site under tight wintertime atmospheric inversions. In contrast, nitro-PAH levels were highest in Riverside during August, as a result of enhanced summertime photochemistry. Hydroxyl radical-initiated reactions produced nitro-PAHs in both seasons, while in winter no evidence for nitrate radical chemistry was seen. For the August samples, nitrate radical-initiated formation of nitro-PAHs is suggested by nitro-PAH isomer profiles not only at the downwind location as anticipated, but also at the source site. In Southern California, the contribution of atmospheric formation to the ambient burden of nitro-PAHs is dominant with the semi-volatile nitro-PAHs being the most abundant and 2-nitrofluoranthene being the major particle-associated nitro-PAH. Here we discuss the evidence for NO_3 radical-initiated nitro-PAH formation in Los Angeles and in Riverside.

Nitro-PAH formation from NO_3 radical reaction

As seen from Figure 1, those nitro-PAHs formed only by OH radical-initiated reactions, 3NBph and 2NP, showed less variation in their summer vs winter ratios to CO than those nitro-PAHs formed by both OH and NO_3 radical-initiated reactions, 1NN, 2NN, MNNs, DMNNs and 2NF [1-3], suggesting that summertime NO_3 radical chemistry contributed to the ambient concentrations of the latter.

In contrast to Los Angeles where the semi-volatile nitro-PAH/PAH and nitro-PAH/CO ratios peaked during the 1100-1430 samples, in Riverside in the summer the NNs, MNNs and DMNNs normalized to CO (see Figure 1) were highest in the overnight

Table 1. Ambient concentrations of PAHs (in ng m^{-3}) and nitro-PAHs (in pg m^{-3}) measured in Los Angeles and Riverside during August 2002 (all times PDT).

	Los Angeles				Riverside			
Compound	**0700–1030**	**1100-1430**	**1500-1830**	**1900-0630**	**0700–1030**	**1100-1430**	**1500-1830**	**1900-0630**
***PAHs* (ng m^{-3})**								
Naphthalene	388.7	152.4	126.6	202.1	300.8	54.8	21.5	148.1
2-MN	166.4	48.2	49.3	86.7	113.4	12.4	6.4	51.1
1-MN	69.4	17.4	17.2	35.5	37.0	4.3	2.4	20.6
2 EN	4.8	1.5	1.7	2.3	3.0	0.8	0.5	1.6
1-EN	1.3	0.5	0.5	0.4	0.9			0.7
2,6/2,7 DMN	8.9	1.8	2.0	4.6	3.4	0.7	0.5	2.7
1,3/1,7 DMN	9.3	1.6	1.8	4.2	3.0	0.6	0.4	2.2
1,6 DMN	5.0	1.0	1.1	2.7	1.9	0.4	0.3	1.8
1,4 DMN	0.9	0.3	0.3	0.4	0.4			0.5
1,5/2,3 DMN	2.2	0.5	0.6	1.2	0.9			0.7
1,2 DMN	1.6	0.4	0.5	0.6	0.7	0.8		0.4
Biphenyl	8.2	3.5	2.4	2.1	6.1	3.6	2.7	2.3
Phenanthrene	14.9	11.6	8.2	5.7	10.5	8.2	7.7	5.3
Anthracene	0.5	0.3	0.3	0.03	0.3	0.1	0.1	0.1
Σ (MePhe)	7.2	7.1	5.7	2.6	4.9	4.3	4.8	1.6
Fluoranthene	2.8	2.2	1.5	1.5	1.4	1.3	1.0	1.1
Pyrene	3.3	2.0	1.8	1.6	1.3	0.8	0.6	0.7
***NPAHs* (pg m^{-3})**								
1NN	237	243	112	152	190	201	142	354
2NN	258	243	90	99	308	273	140	237
2M4NN	10	8	4	10	15	5	9	34
1M4NN+1M6NN	70	66	31	41	64	48	36	55
Σ (MNN)	244	237	108	164	227	167	215	283
Σ (DMNN+ENN)	128	98	49	106	107	61	38	139
3-NBph	64	73	18	32	103	84	82	40
9-NA	64	18	11	36	31	17	34	26
N-Phe	72	46	26	13	60	45	54	19
2NF	131	63	16	41	252	72	30	262
1NP	12	8	3	3	14	4	3	5
2NP	4	1	0.2	1	7	2	0.3	3

Abbreviations: MN, methylnaphthalene; EN, ethylnaphthalene; DMN, dimethylnaphthalene; MePhen, methylphenanthrene; NN, nitronaphthalene; *x*M*y*NN, x-methyl-y-nitronaphthalene; MNN, methylnitronaphthalene; DMNN, dimethylnitronaphthalene; ENN, ethylnitronaphthalene; 3NBph, 3-nitrobiphenyl; 9NA, 9-nitroanthracene; N-Phe, nitrophenanthrenes; 2NF, 2-nitrofluoranthene; 1NP, 1-nitropyrene; 2NP, 2-nitropyrene.

Table 2. Ambient concentrations of PAHs (in ng m^{-3}) and nitro-PAHs (in pg m^{-3}) measured in Los Angeles and Riverside during January 2003 (all times PST).

	Los Angeles				Riverside			
Compound	**0700–1030**	**1100-1430**	**1500-1830**	**1900-0630**	**0700–1030**	**1100-1430**	**1500-1830**	**1900-0630**
***PAHs* (ng m^{-3})**								
Naphthalene	1589.4	757.6	1210.8	1148.7	534.8	109.6	183.4	498.8
2-MN	727.7	310.2	587.0	620.8	287.1	50.5	79.8	240.1
1-MN	306.2	110.2	235.2	363.0	90.6	16.2	29.2	92.0
2 EN	30.2	11.3	22.5	36.5	14.6	3.9	7.8	12.7
1-EN	4.5	2.0	3.5	5.2	2.5	1.5	1.2	1.7
2,6/2,7 DMN	40.3	13.5	33.1	59.2	18.0	4.4	7.9	17.7
1,3/1,7 DMN	40.8	12.7	32.5	61.7	16.6	3.8	6.7	16.8
1,6 DMN	19.4	6.7	15.6	30.5	9.4	2.3	4.0	9.5
1,4 DMN	3.3	1.5	2.6	5.5	2.2	0.8	1.3	1.9
1,5/2,3 DMN	9.6	3.6	8.7	16.4	4.9	1.4	2.7	5.1
1,2 DMN	6.9	2.6	6.1	10.8	3.4	1.1	1.8	2.9
Biphenyl	22.9	15.0	14.5	21.4	10.5	5.4	5.6	10.9
Phenanthrene	17.3	15.1	18.0	15.4	13.5	7.2	12.8	10.5
Anthracene	1.6	0.5	1.2	1.3	0.7	0.1	0.3	0.6
Σ (MePhe)	8.8	8.5	10.2	7.6	7.2	4.5	6.3	4.4
Fluoranthene	6.0	3.4	4.1	3.1	2.4	1.3	2.0	1.7
Pyrene	6.9	3.3	4.9	3.7	2.7	0.9	1.6	1.5
***NPAHs* (pg m^{-3})**								
1NN	111	132	153	100	106	41	178	201
2NN	151	144	130	76	131	53	163	142
2M4NN	10	8	10	9	15	3	10	23
1M4NN+1M6NN	35	48	56	30	30	19	56	45
Σ (MNN)	178	174	214	139	156	76	201	209
Σ (DMNN+ENN)	152	115	130	120	107	34	91	130
3-NBph	138	138	48	26	80	62	86	49
9-NA	12	13	44	20	11	9	50	21
N-Phe	20	44	52	10	16	27	65	15
2NF	112	98	53	34	78	40	60	139
1NP	38	13	12	21	19	8	9	13
2NP	19	5	3	4	6	3	3	5

See Table 1 for abbreviations.

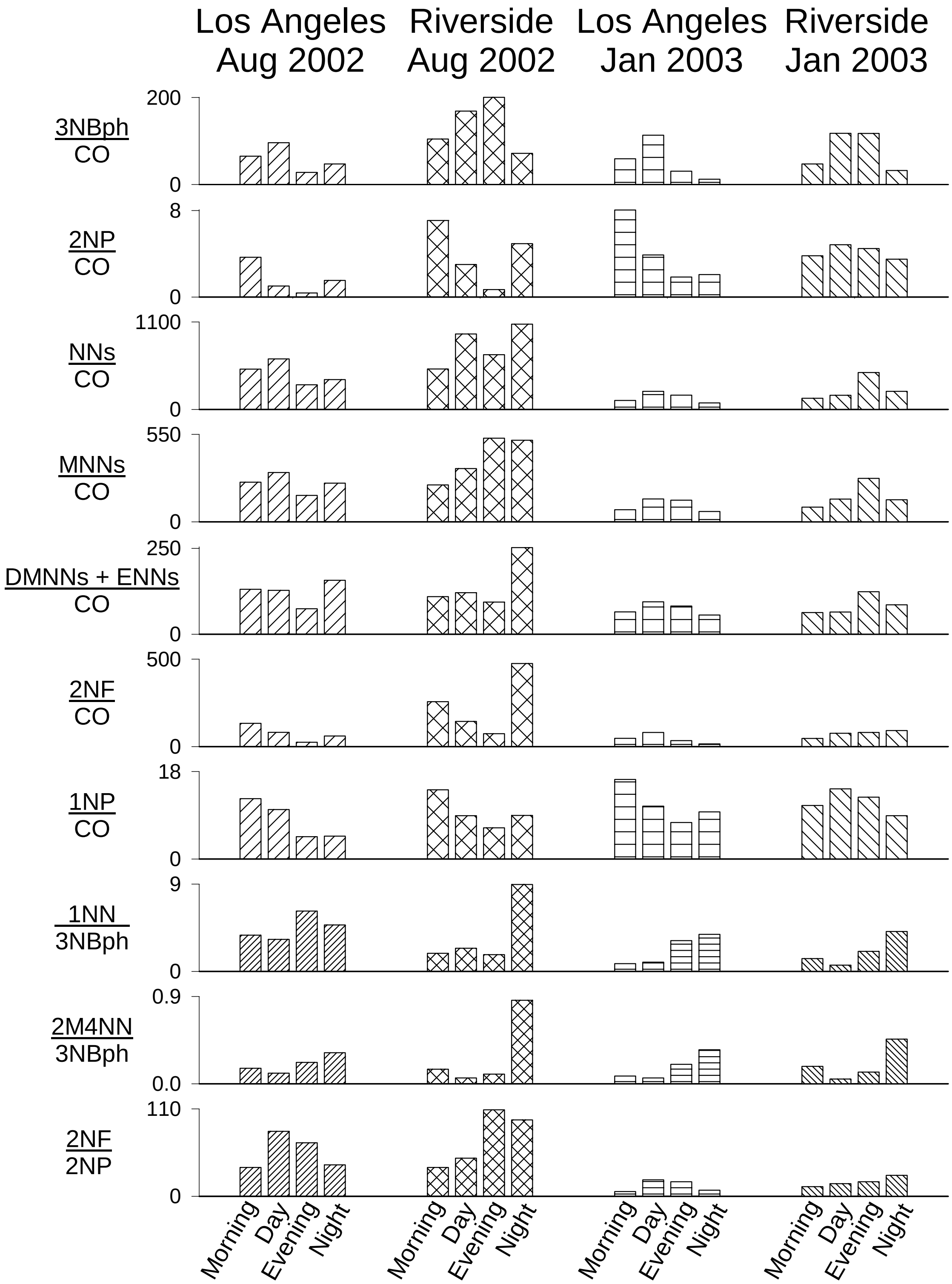

Figure 1. Ratios of [Nitro-PAHs]/[CO] in units of pg m^{-3}/ppm for semi-volatile and particle-associated nitro-PAHs for samples collected in Los Angeles and Riverside and ratios of nitro-PAH pairs with different possible formation mechanisms. (See Table 1 for abbreviations.)

samples and the formation ratios of nitro-PAH/PAH peaked in the "evening" samples. The isomer profiles of the MNNs provide confirmation of NO_3 radical-initiated formation of nitro-PAHs. In the nighttime Riverside sample (Figure 2, bottom mass chromatogram), 2M4NN, 2M1NN and 1M3NN were elevated relative to 1M5NN and 1M4NN+1M6NN when compared with the other samples. The most abundant MNN isomers in all our samples were 1M5NN and 1M6NN+1M4NN, consistent with OH radical chamber reactions of MNs (reacted in a 2:1 ratio of 2MN:1MN, reflecting ambient levels), where highest yields from the OH reactions were measured for 1M5NN, 1M4NN, 1M6NN, 2M5NN, 2M6NN and 2M7NN [2, 4, 5]. As noted above, the MNN profiles in the daytime samples (top and center in Figure 2), match the profile of chamber OH radical reactions [2, 4, 5], except that the isomers that photolyze rapidly, in particular 2M1NN, are lower in the ambient samples. 2M4NN has been reported to be the major isomer formed from the NO_3 radical reactions of 2MN, followed by 2M1NN [2, 5] and 1M3NN has been reported to be the major isomer formed from 1MN [2, 5]. Thus the elevated levels of 2M4NN, 2M1NN and 1M3NN in the nighttime Riverside summer sample (bottom mass chromatogram in Figure 2) indicate the occurrence of NO_3 radical formation. The highest ratios of 1NN/2NN were observed in the nighttime Los Angeles and Riverside samples. Since the ratio of 1NN/2NN is ~1 for the OH radical-initiated reaction of naphthalene and ~2 for the NO_3 radical-initiated reaction [6], this nighttime increase is consistent with NO_3 chemistry occurring, but it should be noted that 1NN also photolyzes more rapidly than 2NN [7, 8].

Since 3NBph is formed only by OH radical reaction, while 1NN is formed by both OH and NO_3 radical reactions of naphthalene and 2M4NN is formed by both OH and NO_3 radical reactions of 2MN, the ratios 1NN/3NBph and 2M4NN/3NBph should increase if NO_3 chemistry occurs. The high values of both ratios observed in the summer, Riverside, nighttime samples (see Figure 1) are consistent with the altered MNN profile noted above, and with our previous reports of NO_3 radical-initiated formation of NNs and MNNs at downwind sites in the Los Angeles air basin [9, 10].

As noted, 2NF is formed by both OH and NO_3 radical reactions, while 2NP is only formed by the OH radical-initiated reaction [1-3]. From environmental chamber studies [11] in which the products of the rate constants (k) for the OH radical-initiated reactions with gas-phase fluoranthene (FL) and pyrene (Pyr) and the nitro-PAH yields (Y) were measured (i.e., $k_{FL}Y_{2NF}$ and $k_{Pyr}Y_{2NP}$), the ratio determined for 2NF/2NP was ~6. Because FL and Pyr are isomers and are generally present in ambient air in nearly equal concentrations (see Tables 1 and 2), their gas-phase concentrations should also be similar and if only OH radical chemistry is considered, the 2NF/2NP formation ratio should be similar to the chamber value of ~6. If NO_3 chemistry occurs in an airmass, the 2NF/2NP ratio will increase.

Widely varying ratios of 2NF/2NP in ambient air have been observed and varying criteria used to distinguish the presence of 2NF formed by NO_3 chemistry [12-19]. Values of 2NF/2NP of 10 or less have most often been observed, while we have reported values as high as 200 for Claremont, CA [14].

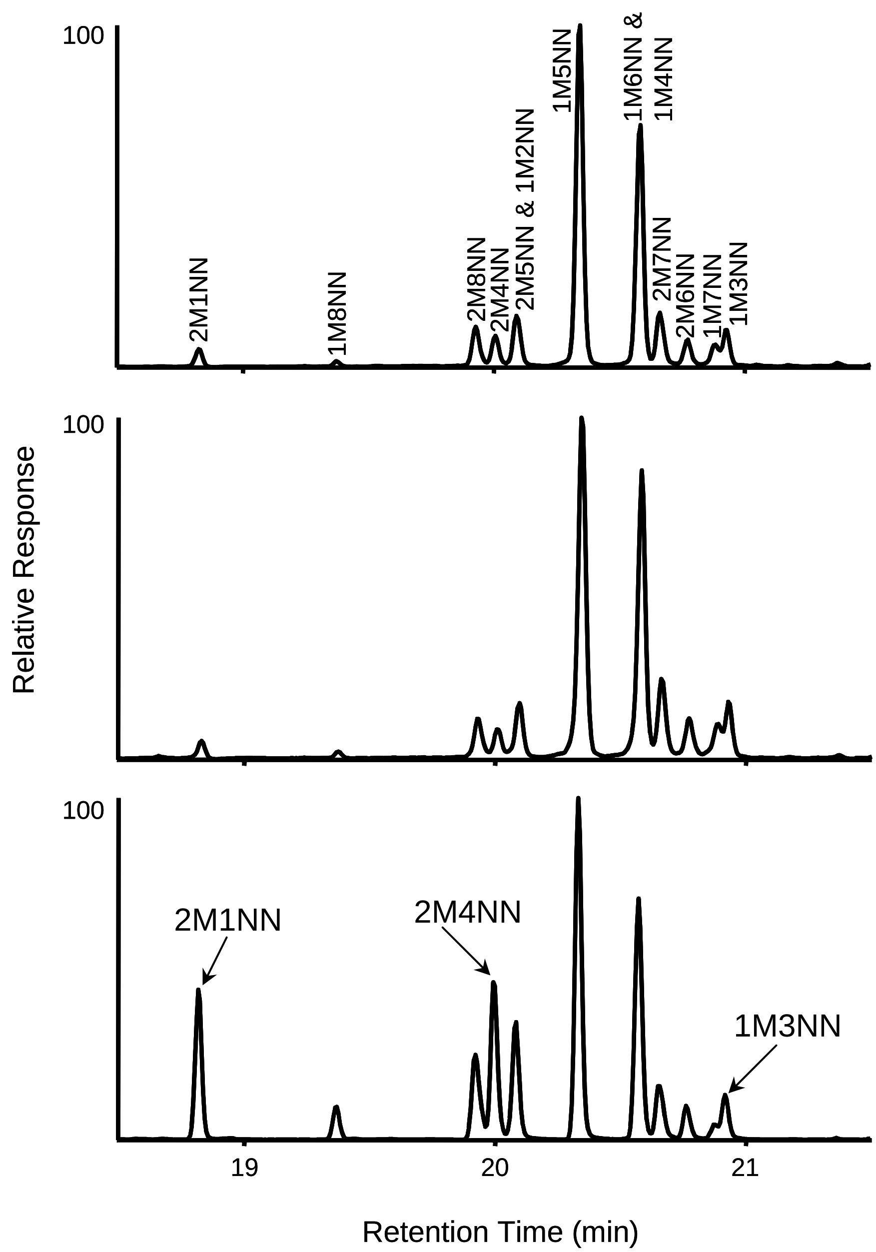

Figure 2. Mass chromatograms for the methylnitronaphthalenes (m/z 187) observed by GC/MS NCI-SIM analysis of composite air samples collected during August 2002: (top) 1100-1430 hr ("Day") samples collected in Los Angeles; (center) 1100-1430 hr samples collected in Riverside; (bottom) 1900-0630 hr ("Night") samples collected in Riverside.

The nitrate radical is formed by the reaction of NO_2 with O_3.

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \qquad (1)$$

$$k_1(298K) = 3.2 \times 10^{-17}\ cm^3\ molecule^{-1}\ s^{-1}\ [20]$$

The NO_3 radical photolyzes during the day, but often both its daytime and nighttime concentrations are limited by the reaction of NO_3 with NO [20].

$$NO_3 + NO \rightarrow 2NO_2 \qquad (2)$$

$$k_2(298K) = 2.6 \times 10^{-11}\ cm^3\ molecule^{-1}\ s^{-1}$$

At ground level, the NO emitted from vehicles also reacts to remove O_3 and, therefore, when NO levels are significant, NO_3 radicals will not be present. It has recently been recognized, however, that an NO_3 gradient increasing with elevation may occur [21] and that significant NO_3 may be present at higher altitudes [22] even when none is present at ground level. Although higher O_3 maxima were reached in Riverside, during the August sampling the NO became non-detectable each night at both sampling locations. Furthermore, O_3 and NO_2 were present at sunset and, therefore, NO_3 formation was expected to occur. In contrast, in the winter at Los Angeles no photochemical production of O_3 occurred and in Riverside the maximum calculated steady-state NO_3 from equations (1) and (2) was < 1pptv.

If the winter nitro-PAHs in the present study were formed largely or solely by OH radical-initiated reactions, the average of the eight 2NF/2NP winter values of 16 ± 7 can be taken as indicative of OH radical-initiated chemistry. The highest ratios of 2NF/2NP were observed in the summer in the Riverside evening (1500-1830; 2NF/2NP = 109) and nighttime (1900-0630; 2NF/2NP = 96) samples. Moreover, the ratios for all of the summertime samples were >35, suggesting that NO_3 radical-initiated reactions contributed to 2NF formation during August at both the Los Angeles site and the downwind Riverside location. The finding of significant NO_3 chemistry occurring in Los Angeles was initially somewhat unexpected, but is, in fact, consistent with the NO_x and O_3 data discussed above.

Directly emitted nitro-PAHs

The photochemically formed nitro-PAHs showed seasonal and spatial variations, with the highest nitro-PAH/CO ratios generally observed in the summer samples at the downwind inland site. The range in the ratio of 1NP/CO was significantly less than that for 2NP/CO or 2NF/CO (see Figure 1), consistent with a direct emission vehicle traffic source for 1NP. Its concentration increased in the winter as a result of lower mixing heights and was not diminished by the reduced photochemistry in January.

As noted, observations similar to this study of the dominance by 2NF of the particle-associated nitro-PAHs have been made at other locations in the U.S.A. [12-14, 18, 23], Europe [15-17, 19, 24] and sites worldwide [15]. Recently, 1NP/2NF ratios >1 were observed in some samples collected in Copenhagen [17]. Additionally, very high 1NP concentrations (up to 42 ng m^{-3}) have been measured in an underground Estonian oil shale mine contaminated by diesel exhaust [25], and 1NP/2NF ratios > 1 have also been observed in roadway tunnels [26]. These data suggest that 1NP concentrations are controlled by emissions from vehicles, in particular from diesel engines, and are influenced primarily by atmospheric dilution.

Fate of nitro-PAHs

The major loss process for gas-phase nitro-PAHs is photolysis [7, 8] and the specific isomer strongly influences the photolysis rate [7, 8]. For example, measurements of the photolysis rate of the NNs and of 11 of the 14 MNNs resulted in calculated life-times ranging from 6 min (for 1M8NN) to 177 min (for 2NN) [calculated for an NO_2 photolysis rate, J_{NO2}, of 0.312 min^{-1}] [8]. Based on modeling 2NF, 1NP and 2NP decay on diesel soot or wood smoke particles in an outdoor chamber, Kamens and co-workers concluded there was little difference in the rate of photooxidation in sunlight based on structure, but they found faster decay on wood smoke particles than on diesel soot particles [27]. The lifetime they determined for photolysis of 2NF on diesel soot [J_{NO2} of 0.312 min^{-1}] was 126 min [27]. Radical chain reactions initiated by reactive carbonyl compounds have been suggested to control the degradation of nitro-PAHs on aerosol particles and it was proposed that degradation may be faster on aged organic aerosols than freshly emitted aerosols [28]. These laboratory studies indicate that the nature of the particles is an important determinant of photolysis rates of particle-associated nitro-PAHs, making extrapolations to ambient conditions uncertain. Also, 2NF has been found at remote locations worldwide, suggesting a long atmospheric lifetime [15].

It appears that evidence for the occurrence of NO_3 radical reactions, based on nitro-PAH formation, is more apparent from the 2NF/2NP ratios than from either differences in the profile of the MNN isomers (Figure 2) or from the ratios of 2M4NN/3NBph or 1NN/3NBph, which only identified the nighttime, Riverside, August sample as obviously influenced by NO_3 radical chemistry (see Figure 1). In the Los Angeles air basin, nighttime elevated polluted layers are known to occur [29-31]. If NO_3 radical chemistry occurred in an elevated layer isolated from ground level NO emissions, 2NF, NNs, MNNs and DMNNs would be expected to be formed and when the morning convective boundary layer exceeded the height of the nocturnal boundary layer they would be mixed downward. The contribution of nitro-PAHs formed by nighttime NO_3 radical reaction to samples collected during the day will depend on how much of the nitro-PAH was formed by NO_3 reaction and its rate of loss due to photolysis. The impact of the NO_3 radical-formed nitro-PAH on the daytime profile will depend on the magnitude of formation from the OH radical reaction. The high 2NF/2NP ratio in all the summer samples suggests that there is indeed a "carry-over" contribution (or in the case of Riverside a "transported" contribution) to daytime 2NF from nighttime NO_3 radical-initiated formation. As seen in Figure 1, the semi-volatile 2-ring nitro-PAHs maximized in Los Angeles during the 1100-1430 "Day" period, while 2NF was higher in the morning than "Day" samples, suggesting that the rate of OH radical-initiated formation of the 2-ring nitro-PAHs is faster than for 2NF (this is consistent with a lower ratio of $[FL]_{Morning}/[FL]_{Day}$ than for the 2-ring PAHs) and/or there was a higher relative contribution (i.e., for NO_3 vs OH radical formation) to 2NF than occurred for the semi-volatile nitro-PAHs.

In addition to an OH radical concentration profile which follows light intensity [32], there can also be a morning spike in OH radical concentration due to early morning photolysis of HONO which built up overnight [33, 34]. If this occurred, 2NF, 2NP, 3NBph, NNs, MNNs and DMNNs would be formed. The presence of enhanced 2NF and 2NP in certain morning samples, and especially of 2NP in the winter in Los Angeles (Figure 1) could be due to HONO photolysis, but the lack of corresponding maxima in 3NBph and other 2-ring nitro-PAHs is difficult to explain. It should be noted that the present samples were not collected with a size-fractionated inlet. Nitro-PAH analyses of size-resolved particles, sampling of nitro-PAHs with greater time resolution and/or at elevated sites, as well as additional laboratory studies of nitro-PAH formation and photolysis could improve our understanding of the apparent differences in behavior seen in this study between the semi-volatile and particle-associated nitro-PAHs.

Clearly, in Southern California and many locals, atmospheric 2NF formation dominates over direct emissions of nitro-PAHs such as 1NP. Despite their rapid photolysis, in southern California and other areas where vehicle emissions of 2-ring PAHs and high levels of photochemical oxidants occur, semi-volatile nitro-PAHs achieve concentrations higher than those of particle-associated nitro-PAHs. Further investigations of ambient nitro-PAHs are needed, in part because formation of short-lived 2-ring nitro-PAHs may "cycle" gas-phase PAHs onto other compound classes, including quinones [35, 36] which may have important toxicological implications [37, 38].

Future Work

As noted above, the particle-associated nitro-PAHs, including 2NF, 1NP and 2NP, were analyzed in samples collected without size-fractionation. Size-fractionated fine and ultrafine particle samples (fine, particles with diameters between 0.18 μm and 2.5 μm and ultrafine, particles with diameters <0.18 μm) were collected at the same times and locations by Drs. Fine and Sioutas and their group. We hope in the next quarter to receive an aliquot of these samples to analyze for, in particular, 2NF and 1NP. As noted, 2NF is attributed to atmospheric formation, while 1NP is believed to be a direct emission. It will be interesting to see if there are differences in size distribution, reflecting their different sources.

Additionally correlations of phthalic acid and 4-methylphthalic acid with the nitro-PAHs will be examined. These compounds were measured by Dr. Fine and co-workers in their size-fractionated samples and they have suggested that these compounds are markers of secondary particle formation. If atmospheric reactions of naphthalene and 2-methylnaphthalene are the source of these phthalic acids in ambient particles their temporal profiles should follow those of other reaction products such as 1- and 2-nitronaphthalene and 2-methyl-*x*-nitronaphthalenes (e.g., 2M6NN and 2M7NN).

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6. Study of Indoor/Outdoor Ultrafine Particles near Busy Freeways

Objective

Because ultrafine particles in urban areas show high spatial variability near sources and because people spend more than 80% of their time indoors, it is necessary to study the levels of ambient ultrafine particles in the indoor environment at hot urban spots, i.e. near freeways. The overall objective of this project is to improve our knowledge of the indoor levels of ultrafine particles from outdoor origin, especially those from motor vehicles in the vicinity of freeways. The basic hypothesis is that the existing indoor/outdoor aerosol penetration models may not be appropriate to predict indoor ultrafine particles levels, because of the unique nature of vehicle emitted ultrafine particles.

Sampling Site

Five two-bedroom apartments in the vicinity of the 405 Freeway in Los Angeles, CA were recruited for this study. Four of the five apartments are on the downwind side of the 405 freeway located from 20-50 m from the edge of the freeway. The remaining apartment is on the upwind side of the 405 Freeway. By arrangement with the tenants, no smoking, cooking, or cleaning activities took place during the sampling periods. The apartments have mechanical ventilation systems that can be turned off. Most sampling during the reporting period was conducted with the mechanical ventilation turned off. This study design provides a unique opportunity to monitor infiltration of particulate matter of outdoor origin into the indoor environment.

Instrumentation

Measurements were made through a common manifold that was switched to alternately sample indoor or outdoor air every 9 min. The switching manifold consisted of a solenoid valves programmed to switch in synchrony with the sampling interval of the instruments. Indoor and outdoor particle size distributions in the size range from 6 nm to 220 nm were measured by a Scanning Mobility Particle Sizer (SMPS 3936, TSI Inc., St. Paul., MN). In each 9-minute sampling period three size distribution samples were taken in sequence with the SMPS. At the same time black carbon concentrations were measured by an Aethalometer and CO concentrations were measured by a TSI Q-trak. Average air exchange rates were measured by means of Harvard CATs samplers. Total particle number concentrations were measured by a TSI P-trak.

Future Work

A Tandem-DMA (TDMA) vehicular particle volatility study will be conducted. The purpose is to determine the degree of volatility of fresh vehicular emissions as a function of particle size. Similar TDMA experiments have sampled ambient air (in the context of nucleation) and vehicular emissions from dynamometer tests. However, ultrafine particle emissions from dynamometer tests have been shown to vary significantly with dilution temperatures, ratios, and residence times. This study will characterize fresh vehicular emissions under real-world conditions downwind of freeways. The results will be used to determine the volatility of fresh emissions, to validate near freeway particle physics models, and to guide future studies on toxicity as a function of particle volatility

A particle size will be selected with the first DMA, and the second DMA will be used to observe the resulting particle size distribution. Input to the second DMA will alternate between heated, open (control), and ambient (to measure the overall size distribution). Particle sizes will be selected in the range from 15 nm to 150 nm

This study will use the apartments of the Indoor/Outdoor Ultrafine Particles study. The tests will therefore include alternate sampling of indoor and outdoor aerosols. The data will help interpret the results from the Indoor/Outdoor Ultrafine Particles. As we move into the winter, these data will become more valuable in terms of PM volatility. More volatile PM is bound to be formed during winter from condensation of organic vapors found in vehicle exhaust than during summer.

7. Chemical Characterization of Ultrafine Particles in the LA Basin

Background

It has been found that ultrafine particles (diameters less than 100 nm) are comparatively more toxic than larger particles with similar chemical composition and mass. Additional studies have demonstrated a dramatic drop of ultrafine number concentrations with increasing distance from busy freeways in the Los Angeles basin, demonstrating that vehicular pollution is the major source of ultrafine particles, and that high particle number can be a local phenomenon. Little is known about how the chemical constituents of ultrafine particles are distributed within the ultrafine size range. The objective of the current study is to give a more complete representation of size-fractionated ultrafine chemical characteristic by sampling across four different locations and multiple seasons in the Los Angeles Basin.

Methods

Fourteen-day composite size-fractionated $PM_{2.5}$ samples, including several ultrafine size ranges, were collected at four sites and three seasons in the Los Angeles Basin. The seasons are defined as: fall 2002 (September – November); winter 2002 (December – February); and summer 2003 (June – August). The first site was at the University of Southern California near downtown Los Angeles. This sampling location is downwind of a major freeway and represents an urban mix of industrial, vehicular and construction sources. The Long Beach station is located on one of the busiest streets in Long Beach, and is located about one half a mile northeast of a major freeway. The Upland site is located in a residential area at least 3 miles away from a major freeway. The sampling location at Riverside is at the Citrus Research Center and Agricultural Experiment Station (CRS – AES), a part of the University of California – Riverside. Riverside is 90 km east of downtown Los Angeles and is primarily a residential and commercial center. Because of the relatively western location and the surrounding urban environment, Long Beach and USC are considered “source” sites where fresh particles are emitted primarily from vehicular and industrial sources. The other sites, Riverside and Upland are designated “receptor” sites where the aerosol is composed of advected, aged and photochemically processed air masses from the central Los Angeles area. The transport time of air masses from source to receptor sites can vary from a few hours to more than a day.A NanoMOUDI (Nano-Micro orifice uniform deposit impactor, MSP Corporation, Minneapolis, MN) impactor collected samples continuously at 10 lpm for a period of two weeks at each site. The NanoMOUDI is a cascade impactor operating under low pressure connected to a MOUDI after the 56 nm cut-point stage and includes three additional stages with cut points of 32nm, 18nm and 10 nm (Marple and Olson, 1999). Measurements of size-fractionated mass, inorganic ions (Sulfate and nitrate), and elemental and organic carbon (EC/OC) were performed on all MOUDI and Nano MOUDI aluminum foil substrate samples

Results and Discussion

Table 1 shows the $PM_{0.18}$ mass and the chemical species in the ultrafine range (diameters less then 180 nm) measured at the source and receptor sites for all seasons. The mass concentrations across all sites and seasons range from 859.79 to 3493.01 ng/m^3. The concentrations during fall are higher as compared to the winter and summer across all the sites. USC, a source site, has the highest ultrafine mass concentration for all the three seasons, from the influence of the heavy traffic associated with the nearby freeway. The chemical composition of ultrafine varied in the range 32-60% Organic Carbon, 1-34% Elemental Carbon, 0-24% sulfate and 0-4% nitrates. At all sites carbonaceous aerosols i.e. sum of EC and OC, are the largest contributor to the ultrafine mass followed by sulfate and nitrate, ranging from 48-80% of the total ultrafine mass concentrations.

Table 1. $PM_{0.18}$ Mass and chemical species concentrations at the source and receptor sites, all seasons

Fall	Mass (ng/m^3)	Sulfate (ng/m^3)	Nitrate (ng/m^3)	EC (ng/m^3)	OC (ng/m^3)
USC	3493.01	203.59	19.96	1191.02	1413.927958
Long Beach	3099.40	153.96	34.99	181.55	1538.008355
Riverside	2888.43	61.21	69.65	704.08	1033.410594
Upland	2865.73	46.64	26.65	153.03	1341.234145

Winter	Mass (ng/m^3)	Sulfate (ng/m^3)	Nitrate (ng/m^3)	EC (ng/m^3)	OC (ng/m^3)
USC	1493.10	0.00	0.00	277.90	901.96
Long Beach	1235.68	130.21	0.00	104.16	710.87

Riverside	1310.64	0.00	0.00	38.29	587.74
Upland	1450.97	0.00	0.00	20.63	1051.11

Summer	**Mass (ng/m^3)**	**Sulfate (ng/m^3)**	**Nitrate (ng/m^3)**	**EC (ng/m^3)**	**OC (ng/m^3)**
USC	2047.52	495.45	0.00	28.14	658.48
Long Beach	859.79	155.56	0.00	15.26	378.09
Riverside	1527.37	209.24	64.27	124.13	508.06
Upland	1417.65	203.17	0.00	65.75	476.08

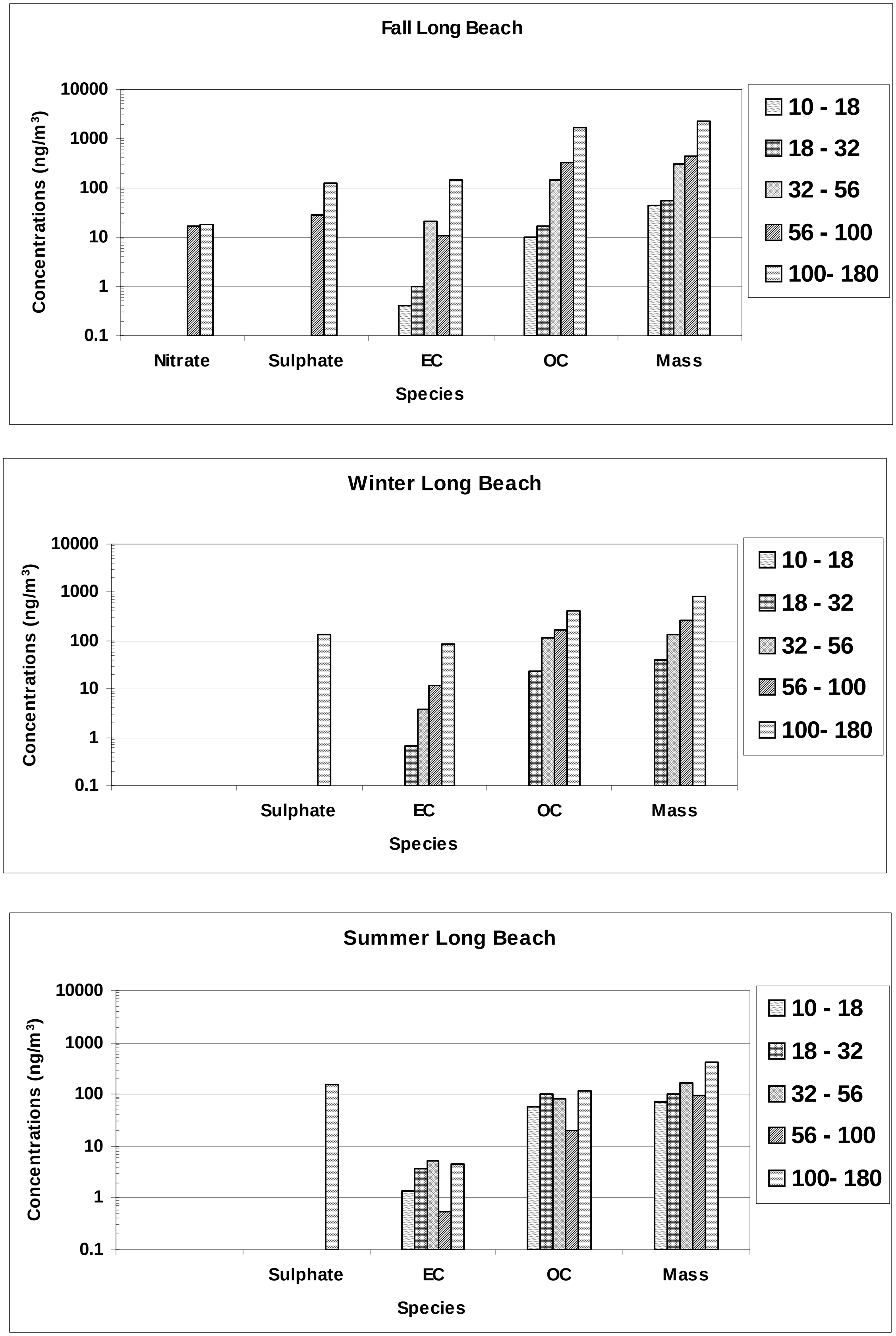
The size distribution of the chemical composition measured at Long Beach for all the three seasons is given in Figure 1. The OC distribution is very similar to the total mass and is the most predominant chemical species. The OC concentration was observed to be the highest in fall with a value of 2153.2 ng/m^3 followed by 710.86 and 378.08 ng/m^3 in winter and summer respectively. In summer, a peak of OC is observed for the 32-56 nm size fraction possibly resulting from summertime photochemical secondary aerosol formation. The size distribution of EC closely follows that of the total mass. The EC contribution to the total mass was observed to be highest during winter, accounting for 8.4% of the mass. Nitrate was found only in fall in the ultrafine range and contributing 1.1 percent of total mass and only in the 56 to 180 nm size range. The sulfate concentration at Long Beach was found to be highest in summer contributing 18% of the total mass. Another important observation is that, sulfate and nitrate are rarely present in the sub 56 nm size ranges for all the seasons.

Figure 2 shows the size distribution of the chemical composition measured at USC in fall, winter and summer. The primary source of atmospheric ultrafine PM at USC is a nearby freeway with heavy diesel and gasoline engine traffic, The percent contribution of OC to the total mass was found to vary from a maximum of 60.4 percent during winter and 32.1 percent summer. The 32 to 56 nm size range exhibited a peak in OC concentration in summer, as was observed at Long Beach, potentially due to photochemical secondary aerosol formation. The EC size distribution also followed the pattern of total mass at USC for all the three seasons. Nitrate was found in 56 to 180 size bins at USC and only during fall. An increase in sulfate concentration was observed during summer compared to winter when sulfate was not detected in the ultrafine range.

The third site, Upland is a receptor site, and the size distribution of chemical species at Upland is given in Figure 3. As was observed in the two previous plots, OC dominates the ultrafine mass and the pattern of size distribution is similar to the total mass size distribution. The OC accounts for approximately 33.58 to 77.44 percent of the total mass in summer and winter respectively. The EC size distribution also followed the pattern of total mass size distribution. Sulfate is found only during fall and summer at Upland in the size range of 56 to 180 nm.

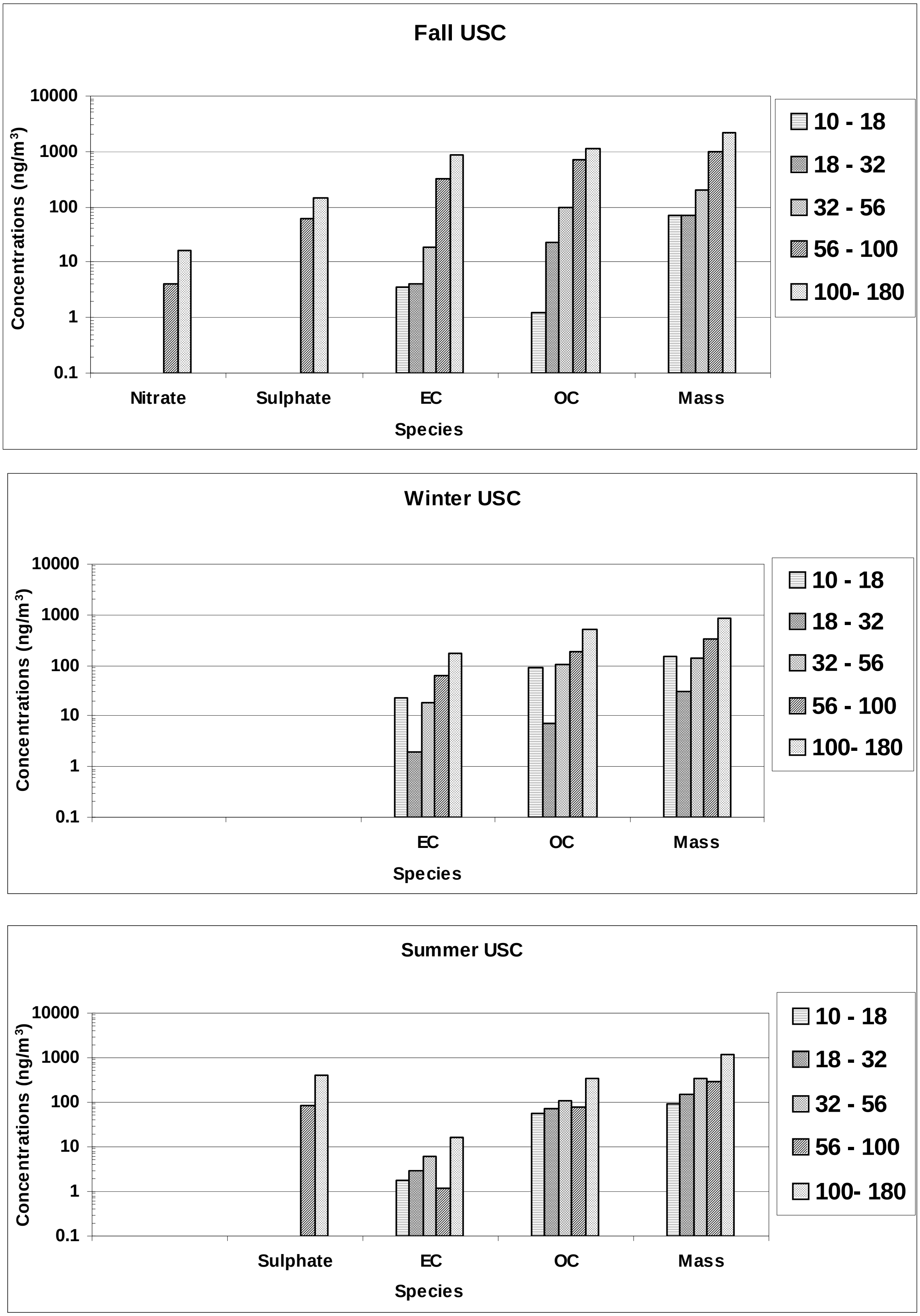
The chemical species size distribution at Riverside is given in Figure 4. The OC size distribution was similar in pattern to the overall mass distribution. OC consisted 50 to 33 percent of the total ultrafine mass at Riverside during fall and summer respectively. In winter the percentage contribution was 44.84 towards the total mass. It was observed that the elemental carbon concentrations in the ultrafine mode at the source sites, USC and Long Beach, are higher in fall and winter due to fresh emissions from diesel traffic. During summer, the EC concentrations were found to be comparatively higher at the receptor sites Riverside and Upland. Summer in Los Angeles is characterized by increased, afternoon, southwesterly winds that carry air masses from the source to the receptor sites. Since particulate elemental carbon is emitted only from vehicular sources, high concentrations of EC at the receptor sites is most likely due to long range transport of particulate matter from sources far upwind. It appears that increased summer wind speed and the advection of polluted air masses overcomes the atmospheric dilution caused by higher mixing heights and unstable meteorological conditions in summer.

Riverside is the only site where particulate nitrate was detected in the 32 to 56 nm size range during fall and 56 to 180 nm size bin in summer. Riverside is located a few kilometers downwind of major ammonia sources at the Chino area dairy farms. Previous studies have shown that nitric acid vapor in polluted air masses reacts with ammonia in this area to produce ammonium nitrate aerosol.



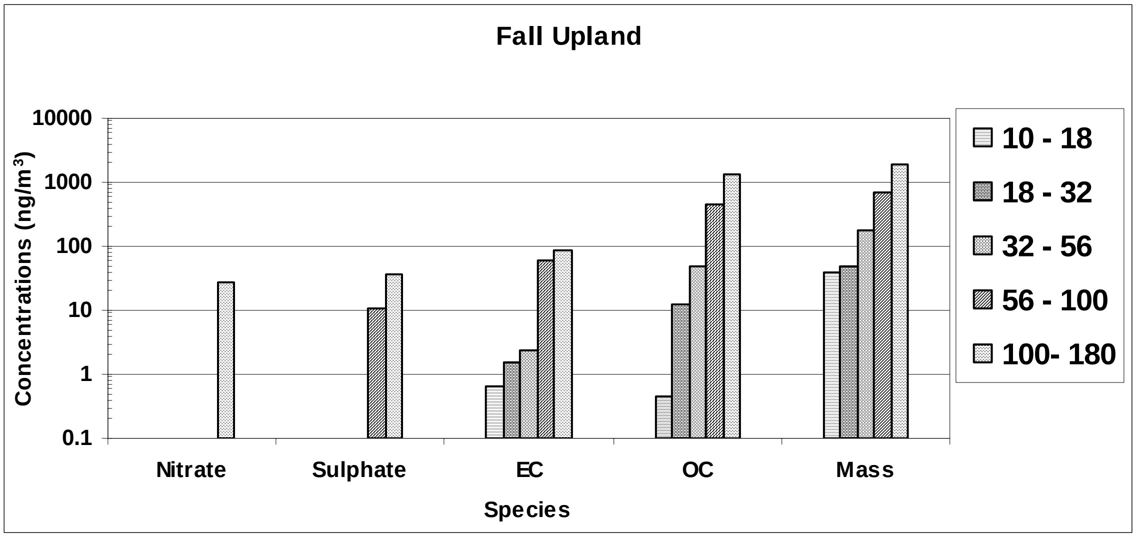
Fall Long Beach
Concentrations (ng/m³)
10000
1000
100
10
1
0.1
Nitrate
Sulphate
EC
OC
Mass
Species
10 - 18
18 - 32
32 - 56
56 - 100
100- 180
Winter Long Beach
Concentrations (ng/m³)
10000
1000
100
10
1
0.1
Sulphate
EC
OC
Mass
Species
10 - 18
18 - 32
32 - 56
56 - 100
100- 180
Summer Long Beach
Concentrations (ng/m³)
10000
1000
100
10
1
0.1
Sulphate
EC
OC
Mass
Species
10 - 18
18 - 32
32 - 56
56 - 100
100- 180

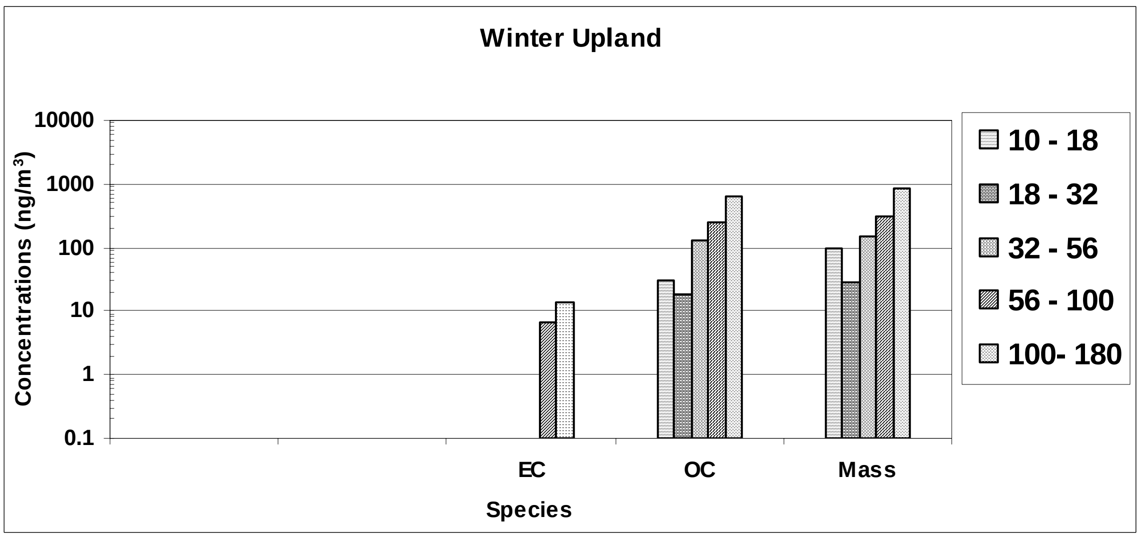
Figure 1



Fall USC
Concentrations (ng/m³)
10000
1000
100
10
1
0.1
Nitrate
Sulphate
EC
OC
Mass
Species
10 - 18
18 - 32
32 - 56
56 - 100
100- 180
Winter USC
Concentrations (ng/m³)
10000
1000
100
10
1
0.1
EC
OC
Mass
Species
10 - 18
18 - 32
32 - 56
56 - 100
100- 180
Summer USC
Concentrations (ng/m³)
10000
1000
100
10
1
0.1
Sulphate
EC
OC
Mass
Species
10 - 18
18 - 32
32 - 56
56 - 100
100- 180

Figure 2


Fall Upland
Concentrations (ng/m³)
10000
1000
100
10
1
0.1
Nitrate
Sulphate
EC
OC
Mass
Species
10 - 18
18 - 32
32 - 56
56 - 100
100- 180


Winter Upland
Concentrations (ng/m³)
10000
1000
100
10
1
0.1
EC
OC
Mass
Species
10 - 18
18 - 32
32 - 56
56 - 100
100- 180

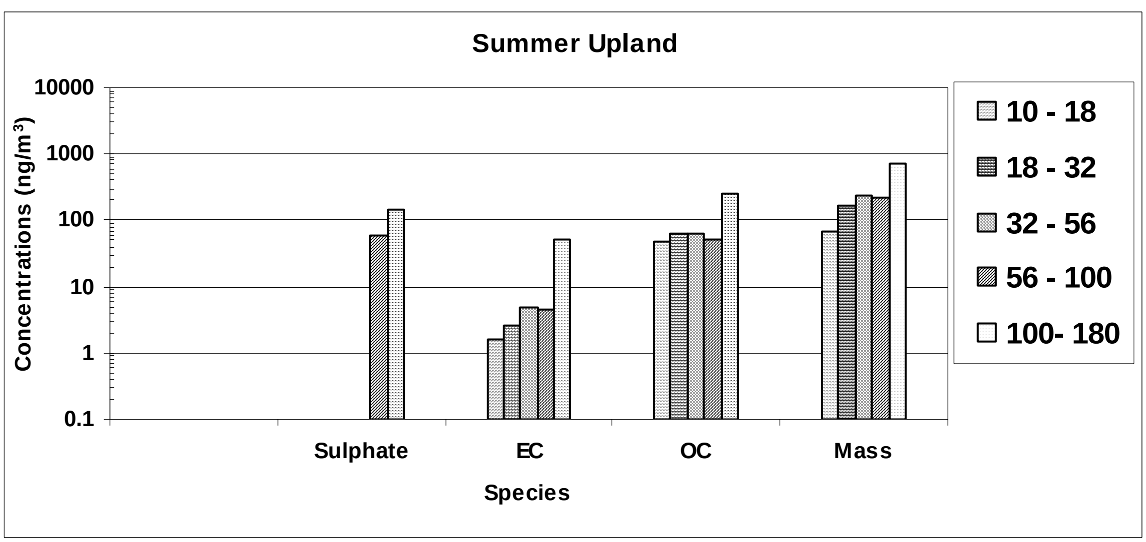
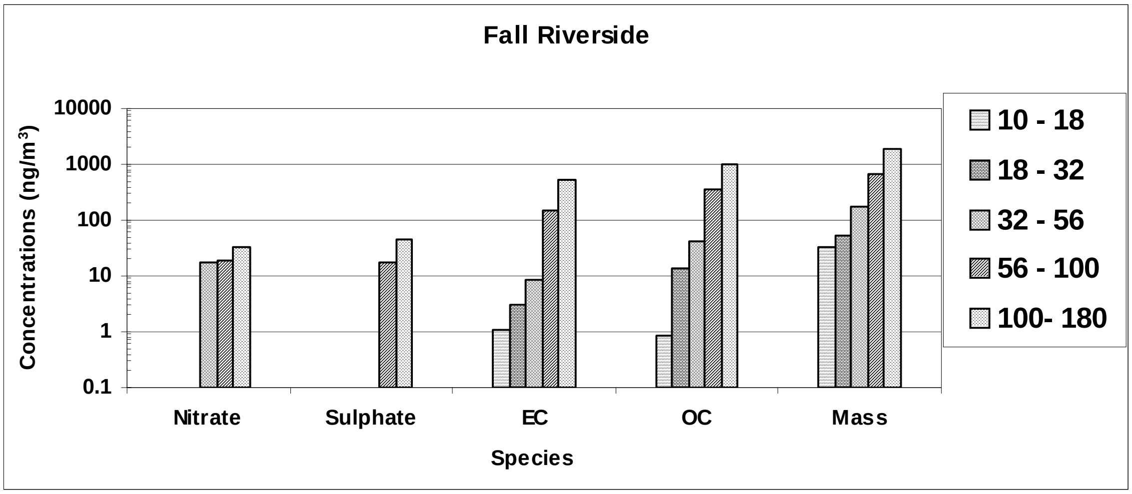
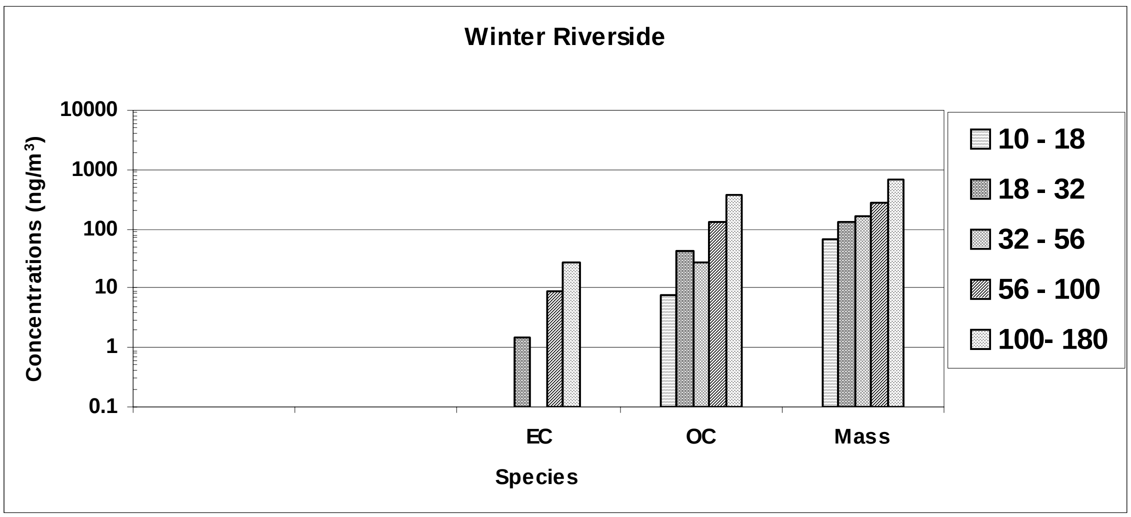

Summer Upland
Concentrations (ng/m³)
10000
1000
100
10
1
0.1
Sulphate
EC
OC
Mass
Species
10 - 18
18 - 32
32 - 56
56 - 100
100- 180

Figure 3


Fall Riverside
Concentrations (ng/m3)
10000
1000
100
10
1
0.1
Nitrate
Sulphate
EC
OC
Mass
Species
10 - 18
18 - 32
32 - 56
56 - 100
100- 180


Winter Riverside
Concentrations (ng/m3)
10000
1000
100
10
1
0.1
EC
OC
Mass
Species
10 - 18
18 - 32
32 - 56
56 - 100
100- 180

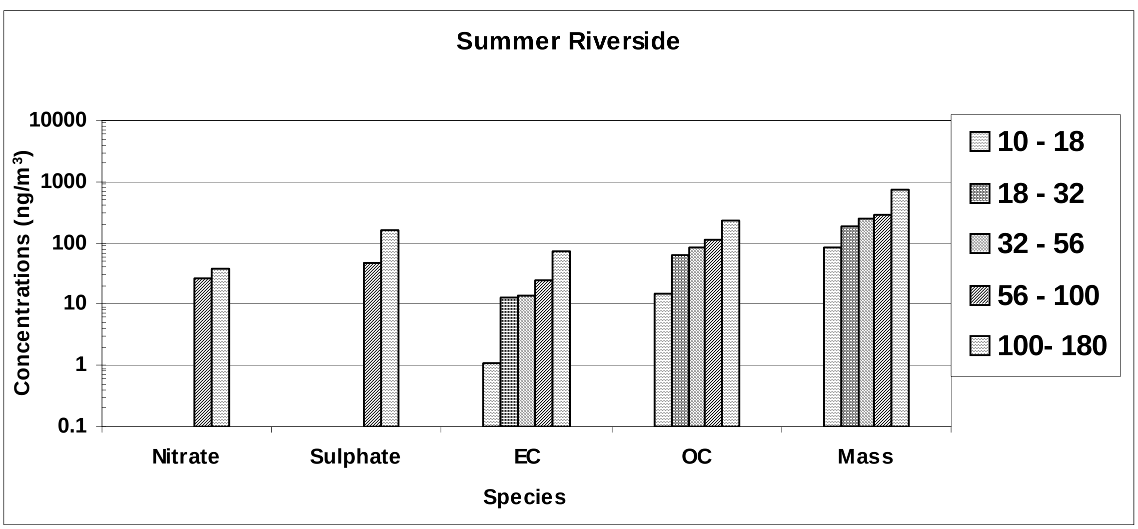

Summer Riverside
Concentrations (ng/m3)
10000
1000
100
10
1
0.1
Nitrate
Sulphate
EC
OC
Mass
Species
10 - 18
18 - 32
32 - 56
56 - 100
100- 180

Figure 4

8. Analysis of Size- and Time-Resolved Particulate Measurements

Aerosol Dynamics Inc.

In our last report, we provided an analysis of the dynamics of the vaporization of nitrate during sampling. With this effort now complete, we are turning to the analysis of the size distributions collected with the cascaded nitrate and carbon systems. In prior reports we have commented on the differences in the mean particle size for nitrate and for carbon, and in the time-variability in the nitrate particle size. For the forthcoming analyses our objectives are (1) to ascertain whether the changes in the size distribution for particulate nitrate are reflected in changes in total physical size distribution (2) to understand the relationship between particle size and meteorology. Specifically, we wish to understand those conditions conducive to formation of nitrate in the condensational mode (<0.45um), droplet mode (0.5 to 1 µm) and coarse mode (1-2.5 µm) respectively.

Our analysis focuses on the data collected in Claremont, California over the one-year period beginning in September 2001. The data set for particulate nitrate consists of 10-min data for in three size fractions: 0.07 µm to 0.45 µm, 0.45 µm to 1.0 µm and 1 µm to 2.5 µm. The data for carbon is in the same three size fractions, but with 30-min time resolution. We have integrated these into a single, hourly averaged data set. Physical size distributions were measured independently by USC, and can provide independent confirmation of the particle sizing indicated from the cascaded nitrate and carbon systems.

The data show that the size distribution for nitrate is more variable than for carbon. In Claremont, $PM_{2.5}$ carbon is consistently dominated by the "condensational" mode while $PM_{2.5}$ nitrate exhibits a seasonal dependence on particle size. In the spring, summer and fall the nitrate size distribution most often shows a dominance of the droplet mode over the condensational mode. During the winter months the nitrate condensational and droplet modes tend to be equally important. For all seasons, there are periods for which coarse nitrate, 1 to 2.5 µm, is important. On some of these days the large nitrate correlates with significant amounts of carbon in the same 1 - 2.5 µm size range.

A summary of the periods of specific interest that we hope to analyze in more detail, in concert with the physical size distribution data are listed in the table below.

Periods of Interest for Particle Size Distribution Analysis

Dates	Nitrate	Particulate Carbon
Oct 11- 21, 2001	Droplet mode dominates on most days, but coarse and condensational modes both significant	Dominated by condensational mode, very little coarse
Jan 16-22, 2002	Droplet and condensation modes comparable	Dominated by condensational mode
Feb 6 - 26, 2002	Large coarse mode on Feb 7, otherwise droplet and condensation comparable.	Large coarse on Feb 7, otherwise condensational mode dominated.

Mar 28 - April 4, April 10 - 15	Droplet mode becomes dominant	While condensational mode still dominant, the droplet mode is more important.

9. Quality Control of Semi-Continuous, Mobility Size-Fractionated Particle Number Concentration Data and 2nd Quarter Data Management

1.

Presentation of "Traffic-Related Emission Factors of two Major Freeways in Southern California" to the "NARSTO WORKSHOP on Innovative Methods for Emission Inventories, Austin, TX on October 15, 2003." Major findings and the summary are as follows:

Motor vehicles are known to emit tremendous amount of ultrafine particles in urban freeways. The particles and other traffic-related air pollutants, such as carbon black and CO, have been shown to decrease with downwind distances from the freeways. Emission factors of these pollutants associated with the traffic in freeways have not been well studied. The goals of this study are three-folds: 1) to test the efficacy of a line-source Gaussian dispersion model on the pollutant concentration decaying away from the freeways; 2) estimate traffic-related emission factors of ultra-fine particles, carbon black, and CO that are released from two major freeways in Southern California, and 3) to relate the emission factors to the characteristic of the freeways.

In addition to collecting meteorological data during sampling time periods, total particle number (by Condensation Particle Counter), ultrafine particle size distribution (by Scanning Mobility Particle Sizer), CO concentration (by Dasibi CO Minitor), and carbon black concentration (by Aethalometer) were collected at two sites, one along I-405 (~ 5% of total traveling vehicles were heavy-duty diesel vehicles) near West Los Angeles and the other beside I-710 (~ 25% of total traveling vehicles were heavy-duty diesel vehicles) near south central Los Angeles. These data were collected at one upwind and 5 to 6 downwind positions in June 15 to July 18, 2001 for the I-405 site and in August 30 to October 27, 2001 for the I-710 site, respectively. A line source Gaussian dispersion model coupling with the concept of mixing zone for roadways was used to model the decaying behaviors of ultrafine particles, carbon black and CO at I-405 and I-710 sites, individually. SAS Proc NLIN was used to estimate model parameters.

Results indicate the model fit well to the decaying behavior of the pollutants, with $R^2 > 0.98$. CO emission factor for the site near I-405, a freeway occupied predominantly with gasoline-powered motor vehicles, was estimated to be 21.7 g per km per vehicle, much greater than 5.3 g per km per vehicle for the site near I-710, a freeway with > 25% vehicles were heavy-duty diesel trucks, consistent with previous studies that gasoline-powered vehicles produce more CO emission. Carbon black emission factor for the I-710 site was estimated to be 0.17 g per km per vehicle, about five-fold higher than 0.035 g per km per vehicle for the I-405 site, consistent with previous studies that diesel-powered vehicles generate more carbon particles than gasoline-powered vehicles. Emission factors of ultrafine particles for the I-405 and I-710 sites were estimated to be 1.08 and 0.60×10^{15} particles per km per vehicle, respectively, confirming both gasoline-powered and diesel-powered vehicles generate tremendous numbers of particles. The unexpected much higher emissions of CO and ultrafine particles at the I-405 site might have resulted from traffic congestion. Further studies should examine the effects of traffic congestion and other factors, such as season, on emission factors.

Planning for the next quarter:

A. Examine effects of traffic congestion on emission factors;
B. Submit a manuscript for publication.

2.

During this quarter, we submitted the following data sets to NARSTO: MOUDI elements at Downey, Riverside, Rubidoux, Claremont, and USC (up to June 11, 2003), USC SMPS (up to June 30, 2003), Partisol elements at USC (up to June 11, 2003), Riverside, Claremont, and Downey.

Planning for the next quarter:

A. Continue to prepare to submit several of the following LA Supersite data sets to NARSTO:
a) Partisol ions and mass; b) MOUDI EC/OC, ions, and mass; c) USC Aethalometer; d) USC meteorological; e) USC APS; f) USC TEOM; g) USC nitrate; h) USC carbon; i) USC BAM.

Status of LA Supersite Data Submitted (Sumission Date) to NARSTO & SIRD

		Claremont		Downey		Riverside		Rubidoux		USC	
		NARSTO	SIRD	NARSTO	SIRD	NARSTO	SIRD	NARSTO	SIRD	NARSTO	SIRD
Partisol	Ions	ND	2002/11/04	ND	2002/11/04	ND	2002/11/04	ND	2002/11/04	ND	ND
	Mass	ND	2002/11/04	ND	2002/11/04	ND	2002/11/04	ND	2002/11/04	ND	ND
	Metal_details	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
MOUDI	ECOC	ND	2002/11/04	ND	2002/11/04	ND	2002/11/04	ND	2002/11/04	ND	ND
	Ions	ND	2002/11/04	ND	2002/11/04	ND	2002/11/04	ND	2002/11/04	ND	ND
	Mass	ND	2002/11/04	ND	2002/11/04	ND	2002/11/04	ND	2002/11/04	ND	ND
	Metal_details	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Aethalometer		2003/05/30	2002/10/25 - hourly 2003/05/30 - 5min	2003/05/30	2002/10/25 - hourly 2003/05/30 - 5min	2003/05/30	2002/10/25 - hourly 2003/05/30 - 5min	2003/05/30	2002/10/25 - hourly 2003/05/30 - 5min	ND	ND
Automet (MetOne)		NA	NA	2003/06/06	2003/06/06	2003/06/06	2003/06/06	2003/06/06	2003/06/06	ND	ND
APS		2003/04/22	2002/04/27	2002/01/24	2002/09/10	2002/03/08	2002/09/10	2002/03/08	2002/09/10	ND	ND
SMPS		8/19/2002 (20010917_20020222)	10/25/2002 (20010917_20020222)	2002/07/22	2002/10/25	2002/08/19	2002/10/25	2002/08/19	2002/10/25	ND	ND
		4/13/2003 (20020326_20020910)	4/27/2002 (20020326_20020910)							ND	ND
TEOM		2003/01/30	2002/04/27	2003/01/30	2002/10/25	2003/01/30	2002/10/25	2003/01/30	2002/04/27	ND	ND
Nitrate		2002/12/10	2002/11/04	NA	NA	NA	NA	2002/12/10	2002/11/04	ND	ND
Carbon		2002/12/10	2002/11/04	NA	NA	NA	NA	NA	NA	ND	ND
R&P Carbon Monitor		NA	NA	NA	NA	NA	NA	NA	NA	ND	ND
BAM		NA	NA	NA	NA	NA	NA	NA	NA	ND	ND
Coarse TEOM		NA	NA	NA	NA	NA	NA	NA	NA	ND	ND

Notes: 1. Data submitted to NARSTO and SIRD were in different formats. 2. SIRD - Supersite Integrated Relational Database
3. Dataram data will not be submit to NARSTO and SIRD, a decision made by Costas and Peter in May 2003. 4. NA: Data were not available or were invalid